



# Impact of organic solvents and common anions on 2-chlorobiphenyl dechlorination kinetics with Pd/Mg

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## ABSTRACT

The current study evaluates Pd/Mg performance for 2-chlorobiphenyl (2-CB) dechlorination in the presence of naturally abundant anions such as sulfate, chloride, nitrate, hydroxide and carbonates and organic solvents that are used for ex-situ PCB extraction or may accompany PCB contamination. While studies abound on the effect of these species on corrosion rates of pure Mg, literature on the behavior of Mg galvanically coupled with Pd remains limited making their investigation necessary. We also provide insights on the effect of initial PCB concentration and system pH on 2-CB dechlorination rates. Among anions studied, especially interesting results were noted for nitrate, bicarbonate and the sodium salt of humic acid.  $\text{NO}_3^-$  underwent reduction to  $\text{NH}_4^+$  thereby competing for electrons and consequently lowering 2-CB dechlorination rate.  $\text{HCO}_3^-$  significantly enhanced 2-CB dechlorination rates by serving as a proton donor. Humic acid also showed faster dechlorination rates, probably by acting as an electron 'shuttle' to the PCB. Only  $\text{OH}^-$  produced significant impairment Pd/Mg reactivity systems. While ethanol and acetone both led to reduced dechlorination rates through reduced hydrogen production and increased affinity of 2-CB for the liquid phase, acetone lowered rates further by undergoing reduction to 2-propanol. 2-CB dechlorination at high solvent concentrations and in the presence of common anions highlights robustness of Pd/Mg systems and suggests they will fare comparably to their bench-scale performance in presence of interferences expected in natural systems.

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## 1. Introduction

An effective system for reductive dechlorination of polychlorinated biphenyls (PCBs), a group of toxic and recalcitrant chlorinated aromatic pollutants [1], has been developed [2–4]. Dechlorination is achieved by magnesium (Mg) particles modified with small amounts of surface-deposited palladium (Pd, 0.02 wt.%). The Pd/Mg bimetallic systems utilize electrons generated by the corrosion of Mg from its galvanic coupling with Pd to drive the dechlorination of PCBs on Pd [2], an excellent hydrogenation catalyst. Recently, we have reported the preferential site of attack and ensuing dechlorination pathways of PCBs on these Pd/Mg systems [4]. In the present study we aim to better understand the relatively unexplored Pd/Mg systems by studying their behavior in the presence of, among others, common anions and organic solvents – parameters relevant in natural systems.

A variety of organic solvents may accompany chlorinated organic contaminants in groundwaters and in waters overlying the sediments and in their interstitial pores. In case of ex-situ washing

of soils and sediments contaminated with PCBs, solvents with high affinity for PCBs such as ethanol and acetone are used for their extraction, generating concentrated wastes that need to be treated further to limit their toxicity before disposal in confined facilities [5–7]. However, organic solvents when present in significant proportions will lower the polarity of water, reducing its readiness for electrolysis with bimetallic systems. This in turn reduces hydrogen production critical for PCB dechlorination [6]. Also, organic solvents increase the affinity of PCBs for the liquid phase, thereby slowing down dechlorination – a reaction taking place on the Pd surface [8]. Some solvents may even compete with PCBs for reduction at active Pd sites adversely affecting PCB dechlorination rates as found in our study.

Meanwhile, naturally abundant inorganic anions such as nitrate, sulfate, chloride, carbonate and phosphate may affect the rate of corrosion by serving as proton donors or electron shuttles, attacking Mg surface, competing for electrons, forming dense corrosion films or at the very least by increasing the ionic strength, and thereby altering PCB dechlorination rates [9–13]. An increased corrosion rate may not always translate into an increase in PCB dechlorination rate, largely depending on how efficiently the hydrogen generated can be utilized. Among naturally abundant inorganic anions, chloride and sulfate are known to be aggressive

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and attack Mg readily [10,11,14], the corrosion rate increasing rapidly with anion concentration. Even though Mg corrosion, unlike that of most metals, is unaffected by dissolved oxygen, the Mg surface is readily attacked by dissolved carbon dioxide or carbonate ions [11,12]. While there have been studies on the effect of anions on corrosion rates of pure Mg [9–12], literature on the behavior of Mg galvanically coupled with Pd is very limited. In fact, Mg with small amounts of cathodic impurities including iron, copper, nickel [9,14,15] can have drastically altered corrosion properties, the impurities behaving as numerous localized cathodes causing accelerated Mg corrosion. Since corrosion of Mg brings about PCB dechlorination while also governing its rate, a thorough investigation into the effect of common anions in Pd/Mg systems is necessary, as it remains undocumented so far.

To summarize, the primary objective of the study is to evaluate the performance of Pd/Mg systems for PCB dechlorination in the presence of: (i) anions including, but not limited to, sulfate, chloride, nitrate, hydroxide and bicarbonates commonly found in natural systems and (ii) ethanol and acetone as representative organic solvents that are used for ex-situ PCB extraction or may accompany PCB contamination.

## 2. Experimental

### 2.1. Synthesis of Pd/Mg

A simple wet-chemistry procedure was used to reductively deposit Pd<sup>0</sup> onto Mg by intimately mixing it with a palladium nano-particle precursor in ethanol. Addition of polyvinylpyrrolidone (PVP), a capping agent enabled formation of nano-scaled Pd islands on Mg thereby providing enhanced catalytic activity at drastically reduced catalyst requirements. The procedure is described in detail elsewhere [4].

### 2.2. PCB dechlorination studies

In a typical experiment, Pd/Mg particles were weighed out in 60 mL clear glass vials with septa caps and 50 mL of a 4 mg/L solution of 2-chlorobiphenyl (2-CB) was added. The 2-CB solution had anions or organic solvents added or varied in 2-CB concentration depending on the specific objective. The vials were tumbled at 40 rpm on a tumbler (ATR) to achieve mixing. Samples were taken at pre-determined times with 1 mL air-tight syringes through the septa for closed-system reaction conditions. The samples were collected in 4 mL glass sample vials with PTFE-lined caps pre-filled with 1 mL of hexane and were extracted into the hexane by shaking on a touch mixer for 1 min. The aqueous and organic phases were separated by centrifuging at 6000 rpm in a centrifuge for 1.5 min. The water-free organic phase (0.5 mL) was pipetted out, spiked with 10 µL of the internal standard (200 ppm D-8 Naphthalene in dichloromethane, Accustandard) and analyzed in the GC/MS. The GC/MS was equipped with a Supelco SPB-5 30 m × 0.32 µm × 0.25 µm column; the calibration curves had  $R^2$  of greater than 0.999 based on eight-point data; the method detection limit was 50 µg/L. All dechlorination experiments were conducted in ambient conditions without any precautions to exclude oxygen. Mass balance was performed using 2-CB and BP concentrations and was found to be 80% or better in each case.

### 2.3. Turbidimetric method for NH<sub>3</sub>-N

Turbidimetric analysis was conducted using a portable colorimeter (Model No: DR/890, HACH Co.) to quantify the presence of NH<sub>3</sub>-N. The Nitrogen, Ammonia Salicylate Method 10031 as described in the HACH manual was followed. The main reactions were: ammonia compounds combine with chlorine to

form monochloramine; monochloramine reacts with salicylate to form 5-aminosalicylate; the 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound; the blue color is masked by the yellow color from the excess reagent present to give a green-colored solution; test results are measured at 655 nm.

### 2.4. Detection of 2-propanol

Qualitative analysis of 2-propanol in acetone/water was conducted using TMCS (trimethylchlorosilane) a silylating reagent. Samples were analyzed on a 6890/5973 GC/MS using a HP-VOC column in a 17 min run starting at 50 °C with a 3 min hold and then ramping to 180 °C followed by a 5 min hold.

## 3. Results and discussions

The Pd content of the particles was 0.02% (w/w, Pd/Mg) as determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The surface morphology of Mg particles (44 µm or smaller) as captured by transmission electron micrographs (TEM) showed the deposition of numerous Pd islands in the nano- and sub-micron range on the Mg surface. Detailed characterization is discussed elsewhere [4].

### 3.1. Effect of Pd/Mg loading

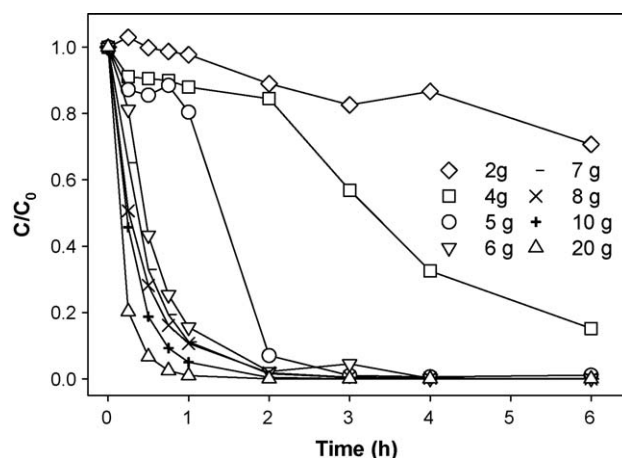
Dechlorination experiments were conducted with Pd/Mg loadings ranging from 2 to 20 g of the bimetal per liter of the 2-CB solution. As seen from Fig. 1, loadings 6 g/L and above produce complete dechlorination within 6 h. A loading of 4 g/L produces close to 85% dechlorination in 6 h. Based on the dechlorination profiles, 4 and 6 g/L bimetal were chosen as candidate loadings for the study.

### 3.2. Effect of organic solvents

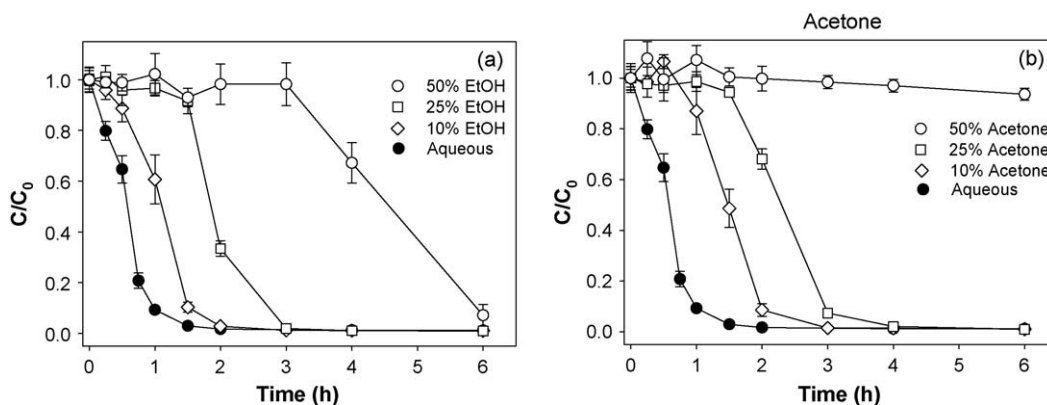
This study was performed in triplicate with 6 g/L Pd/Mg loading, the concentration of solvents varying as 10%, 25% and 50%. Aqueous 2-CB solution without any organic solvent was used as a control.

#### 3.2.1. Ethanol

With increasing amounts of ethanol in the matrix – from 10% through 50% – the dechlorination progressively slows as seen in



**Fig. 1.** Dechlorination with Pd/Mg loadings ranging from 2 to 20 g of the bimetal per L of the 2-CB solution. Initial 2-CB concentration was 4 mg/L, 50 mL of the solution was used and the 60 mL reaction vials were tumbled at 40 rpm to achieve mixing. The lines connecting the sampling events are not fits but meant to guide the eye.

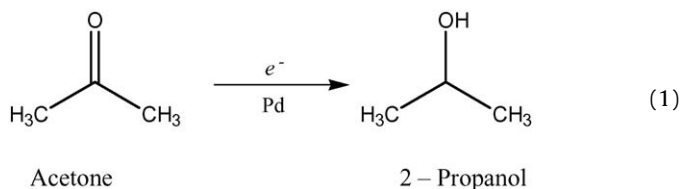


**Fig. 2.** This set performed with 6 g/L Pd/Mg loading, shows dechlorination progressively slowing down in matrices with 10% through 50% (a) ethanol and (b) acetone. At high concentrations, organic solvents cause reduced hydrogen production and increased affinity of 2-CB for the liquid phase. The slowdown was more severe for acetone due to its lower dielectric constant and its reduction to 2-propanol, an undesirable reaction that competes for electrons and/or reactive sites with 2-CB, adversely affecting its dechlorination.

**Fig. 2a.** An organic solvent such as ethanol when present in significant proportions lowers the polarity of water [8], reducing its readiness for electrolysis. This in turn reduces hydrogen production critical for PCB dechlorination. For units with 50% ethanol, there appears to be a lag phase in the first 3 h where the 2-CB concentration remains fairly constant. The initial lag phase is followed by a steady reaction where the 2-CB concentration is seen to drop to almost zero in the next 3 h. This lag phase or incubation period may correspond to the time required to generate a certain minimum amount of hydrogen before dechlorination can commence. This phenomenon has been reported by Devor et al. [16] in their study on mono-substituted PCBs with Pd/Mg in different co-solvents.

### 3.2.2. Acetone

Similar trends as in case of ethanol were observed for acetone (Fig. 2b) due to the same reasons – reduced hydrogen production and increased affinity of 2-CB for the liquid phase. However, on comparing the dechlorination profiles in 10%, 25% and 50% of the two solvents, it can be seen that acetone led to slower rates than same amounts of ethanol (Figs. 2a and b). This may be attributed to a lower dielectric constant of acetone as compared to ethanol which reduces hydrogen production to a greater extent causing slower 2-CB dechlorination. Further, at 50% solvent concentration, the reaction was almost completely inhibited in acetone while the unit with 50% ethanol produced complete dechlorination in 6 h. One hypothesis was that acetone may be undergoing reduction to form 2-propanol and hence competing for reactive sites with 2-CB, adversely affecting its dechlorination. To test the theory, we performed qualitative analysis of 2-propanol in acetone/water using TMCS (trimethylchlorosilane) a silylating reagent. TMCS was observed at 7.8 min with an  $m/z$  of 93 (expected ion of 108 with a loss of 15: the  $-\text{CH}_3$  group) and compares closely to a spectrum in the Spectral Database for Organic Compounds (SDBS no. 10585). Samples spiked with 2-propanol and experimental samples analyzed showed an  $m/z$  of 117 (expected ion of 132 with a loss of the  $-\text{CH}_3$  group) at 9.5 min confirming the reduction of acetone to 2-propanol. A similar instance of reduction of chloroacetone to 1-chloro-2-propanol as well as acetone to 2-propanol over supported Pd has been reported recently [17].



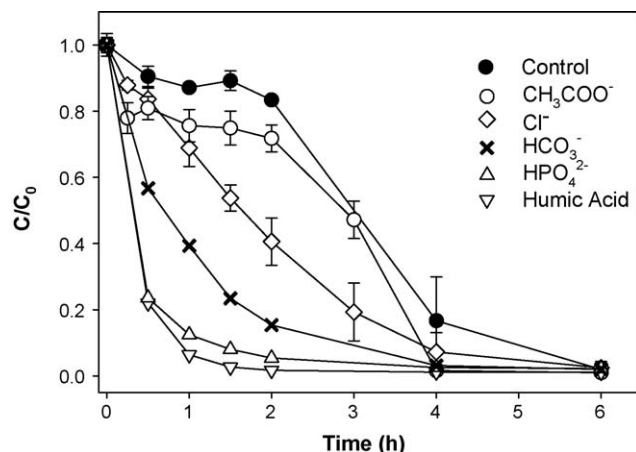
### 3.3. Effect of common anions

The discussion on the effect of anionic species common to natural systems has been divided into three categories – anions that (i) enhance, (ii) enhance and then retard and (iii) retard dechlorination rates as compared to the aqueous control. A Pd/Mg loading of 4 g/L was used in this set of experiments and all anions were from the corresponding sodium salt to limit any interference from cations. All anions were used at 50 mM concentration in 50 mL of 4 mg/L 2-CB solutions.

#### 3.3.1. Enhancement role

$\text{CH}_3\text{COO}^-$ : Addition of acetate leads to increased rate of dechlorination compared to that in pure aqueous medium (Fig. 3). This may be attributed to the extremely high solubility of magnesium acetate (500 g/L) [18] as compared to  $\text{Mg}(\text{OH})_2$  ( $9.6 \times 10^{-3}$  g/L) [14] leading to rapid dissolution of Mg as  $\text{Mg}(\text{CH}_3\text{COO})_2$ . Further, acetate increases conductivity of the solution which means enhanced Mg corrosion rates at the Pd/Mg galvanic cells.

$\text{Cl}^-$ : Chloride is known to attack the protective  $\text{Mg}(\text{OH})_2$  film locally, causing pitting corrosion. Even small amounts of  $\text{Cl}^-$  are known to break down the film [9,10], the corrosion rate increasing



**Fig. 3.** Anions that enhance the dechlorination rate of 2-CB with Pd/Mg systems. Pd/Mg loading of 4 g/L and anions from the corresponding sodium salt at 50 mM concentration in 50 mL of 4 mg/L 2-CB solution were used. Enhancement in dechlorination rate was due to one or more of: anions acting as a steady proton source or electron shuttles, attacking Mg surface causing rapid corrosion or due to rapid dissolution of the protective film through the formation of highly soluble Mg salts.

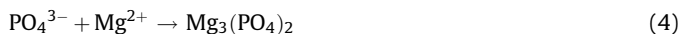
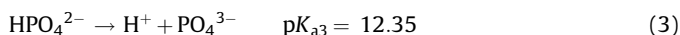
rapidly with  $\text{Cl}^-$  concentration. Song et al. [9] have proposed that  $\text{Cl}^-$  aids in the formation of  $\text{Mg}^+$  – a crucial intermediate in dissolution of Mg. The extremely high solubility of  $\text{MgCl}_2$  (>500 g/L) further destabilizes the film of insoluble  $\text{Mg}(\text{OH})_2$  allowing Mg to corrode and enter into solution as the chloride, making the surface active and causing further dissolution of Mg [19]. The enhanced corrosion of Mg in presence of  $\text{Cl}^-$  is evidenced in Fig. 3 where the PCB dechlorination rate is significantly higher compared to the control.

$\text{HCO}_3^-$ : Since all experiments were conducted under ambient conditions, carbonates are expected to be extremely important species. Aqueous systems with Mg rapidly attain the pH of ~10.5, corresponding to that of a saturated solution of  $\text{Mg}(\text{OH})_2$ . Under ambient conditions, carbon dioxide will readily dissolve in water, and at a pH nearing 10.5 will exist as a mixture of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  [11].



Hence,  $\text{NaHCO}_3$  was added to investigate the influence of  $\text{HCO}_3^-$  on Mg corrosion rate. From Fig. 3 it can be seen that the dechlorination rate underwent significant enhancement in the presence of  $\text{HCO}_3^-$  as compared to the control system with no added  $\text{NaHCO}_3$ .  $\text{HCO}_3^-$  acts as a proton donor attacking the  $\text{Mg}(\text{OH})_2$  film [13], and may also form soluble products with Mg such as  $\text{Mg}(\text{OH})(\text{HCO}_3)$  [20] and  $\text{MgCO}_3$  (Solubility of 0.39 vs.  $9.6 \times 10^{-3}$  g/L of  $\text{Mg}(\text{OH})_2$ ), especially the latter as it is the most stable form of carbonate with Mg in ambient conditions [12]. These two factors lead to accelerated corrosion of the protective  $\text{Mg}(\text{OH})_2$  film, leading to increased PCB dechlorination rates. In fact, studies [11,12] have shown the rate to be proportional to  $\text{HCO}_3^-$  concentration for corrosion of pure Mg. So while the corrosion rates of Mg are practically unaffected by dissolved oxygen, the dissolution of  $\text{CO}_2$  from air can cause accelerated corrosion and thereby enhanced dechlorination.

$\text{HPO}_4^{2-}$ :  $\text{HPO}_4^{2-}$  acts as a proton source aiding in Mg corrosion. From an initial pH of 9.3 of the 50 mM  $\text{Na}_2\text{HPO}_4$  solution, pH rapidly rises to 10.5 from the corrosion of Mg. In this range of pH (9.3–10.5), practically all phosphate exists as  $\text{HPO}_4^{2-}$  (>99%). Small amounts of  $\text{PO}_4^{3-}$  forming as a result of dissociation of  $\text{HPO}_4^{2-}$  combine with  $\text{Mg}^{2+}$  to form magnesium phosphate. Part of this  $\text{Mg}_3(\text{PO}_4)_2$  precipitates as a corrosion film on the Mg surface. However, due to the low solubility of  $\text{Mg}_3(\text{PO}_4)_2$  ( $2.6 \times 10^{-3}$  g/L), we speculate that the recombination will be slow, keeping the dissociation reaction going at a slow but steady rate. Hence,  $\text{HPO}_4^{2-}$  may be acting as a steady source of  $\text{H}^+$  by the following reaction.



**Humic acid:** As shown in Fig. 3, the dechlorination rate of 2-CB was drastically enhanced in the presence of 10 mg/L of the humic acid salt. We confirmed 2-CB dechlorination by documenting the complete conversion of 2-CB to biphenyl. This was somewhat unexpected as natural organic matter is often thought of as a component strongly favored for non-reactive adsorption and hence ‘protection’ of hydrophobic contaminants such as PCBs. However, the revelation of humic substances as an electron shuttle in environmentally relevant reduction processes [21–23] makes their influence on 2-CB dechlorination very interesting. Primary functional groups in humic substances – quinones, carboxylic acids, alcohols, and ketones [21,24,25] act as soluble electron carriers facilitating the reduction of pollutants by accepting electrons from Pd/Mg and ‘shuttling’ the electrons to the pollutant. Hence, in addition to the direct reduction of PCBs by Pd/Mg, an

indirect electron transfer via humic acids may also take place [24] leading to accelerated rates of 2-CB dechlorination.

### 3.3.2. Enhancement and then retardation role

The following three species exhibit this behavior, attacking Mg although due to different properties:

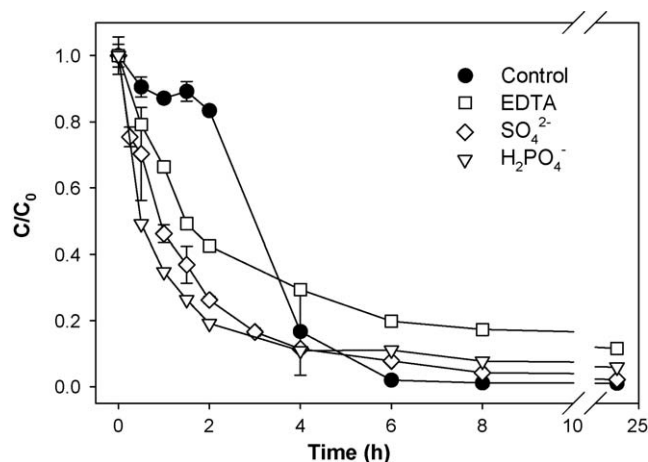
**EDTA:** EDTA is routinely used to remove magnesium ions from hard water or in industrial cleaning [26]. Being a chelating agent, it readily couples with  $\text{Mg}^{2+}$  (being formed by the anodic dissolution of Mg) providing it with an alternate route to enter the solution than combining solely with  $\text{OH}^-$  (being produced at the cathode). This brings about accelerated dissolution of Mg and hence rapid 2-CB dechlorination in the first 2 h. However, at the given molar ratio of elemental EDTA and Mg, we hypothesize that EDTA forces a majority of the Mg into solution by 6 h effectively stopping the dechlorination reaction from that point on as seen in Fig. 4.

$\text{SO}_4^{2-}$ : Sulfate is known to attack Mg surface although it is a mild corrosion stimulator [12] compared to chlorine which corrodes Mg vigorously as discussed before. This may be attributed to the thick film formed in presence of sulfates which reduce the corrosion rate [9,11]. Baril et al. showed the formation of a thick film within 3.5 h of immersing pure Mg into a 0.1 M  $\text{Na}_2\text{SO}_4$  solution. However, the porous nature of the film was not found to completely inhibit the corrosion. Our results indicate similar phenomena as we saw rapid dechlorination in the first 4 h followed by a slow but sustained degradation of 2-CB (Fig. 4).

$\text{H}_2\text{PO}_4^-$ :  $\text{NaH}_2\text{PO}_4$  acts a proton donor releasing  $\text{H}^+$  that attack the Mg surface causing accelerated corrosion and hence enhanced dechlorination of 2-CB for the first 4 h (Fig. 4). However, the rate eventually decreased and reached a plateau indicating that  $\text{H}_2\text{PO}_4^-$  behaves differently from  $\text{HPO}_4^{2-}$  which steadily increased the dechlorination rate. While we were unable to account for the dissimilarity in the corrosion stimulation behavior of the two anions, one reason could be that at such low initial pH (~4),  $\text{H}_2\text{PO}_4^-$  consumes Mg rapidly, slowing down the dechlorination rate after 4 h as seen in Fig. 4.

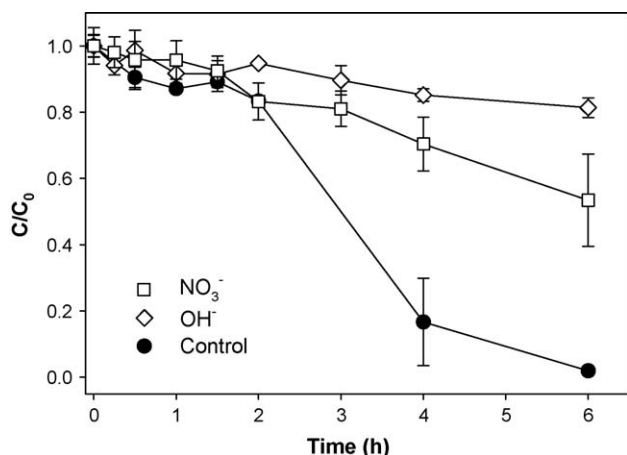
### 3.3.3. Retardation role

$\text{NO}_3^-$ : Nitrate is known to be a corrosion stimulant for Mg [12,14] and could be expected to enhance 2-CB dechlorination rates in a manner similar to chloride. However, significant



**Fig. 4.** Anions that enhance the dechlorination rate of 2-CB followed by its deceleration. Data for 24 h run is shown to demonstrate the eventual slowing down of dechlorination rates after 6 h or so of reaction. Pd/Mg loading of 4 g/L and anions from the corresponding sodium salt at 50 mM concentration in 50 mL of 4 mg/L 2-CB solution were used. Initial enhancement in dechlorination rates occurred from the anions attacking the Mg surface, although by different routes. Eventual plateau in rates was seen due to rapid dissolution of Mg from chelation or formation of dense films of corresponding Mg salts which slowed further corrosion.





**Fig. 5.** Anions that retard the dechlorination rate of 2-CB with Pd/Mg systems. Pd/Mg loading of 4 g/L and anions from the corresponding sodium salt at 50 mM concentration in 50 mL of 4 mg/L 2-CB solution were used. Dechlorination rates were lower (compared to the aqueous control) due to the formation of thick insoluble  $\text{Mg}(\text{OH})_2$  film preventing further corrosion or by anions competing for generated electrons to undergo reduction.

reduction in the dechlorination rate was observed with nitrate (Fig. 5) indicating that nitrate may be getting reduced and hence competing for electrons being generated by Mg corrosion. In fact, zero valent metals including iron, aluminum [27,28] and magnesium [29] have been known to reduce nitrate to nitrite, nitrogen, ammonium and ammonia depending upon experimental conditions. Hence, we tested our hypothesis by analyzing kinetic samples for nitrite (one of the initial reduction products) in an ion chromatograph (IC) and ammonia (a final product of nitrate reduction) using the Salicylate Method 10031 using a portable colorimeter. Nitrite could not be detected as it is a relatively unstable specie under ambient conditions and more importantly because it is a transient intermediate to further reduced products, not seen to significantly accumulate in the system [28]. The samples tested positive for ammonia which is the predominant form of occurrence of the  $\text{NH}_4^+ - \text{N}$  (~95%  $\text{NH}_3$ ) at a pH of 10.5 as per Eq. (5) [29]:

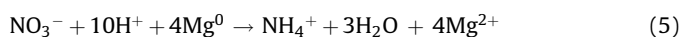
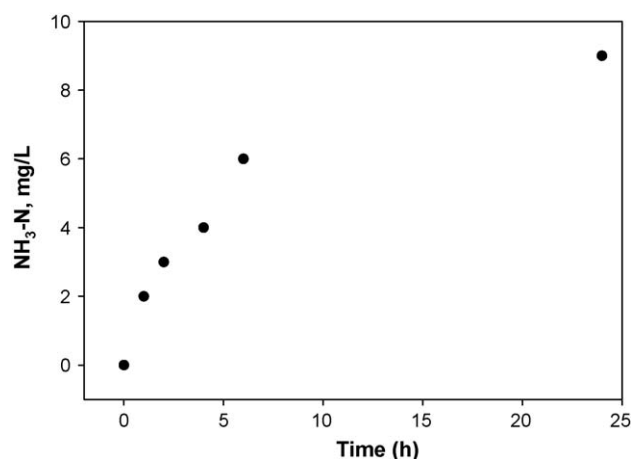


Fig. 6 shows the increasing amounts of the ammonia detected in the system as the reaction progressed. Thus nitrate undergoes chemical reduction all the way to ammonium, competing for electrons and thus slowing down the dechlorination rate.

$\text{OH}^-$ : In alkaline media above pH 10.5, Mg forms a thick  $\text{Mg}(\text{OH})_2$  film on the surface making it very resistant to corrosion [14]. This can be seen in Fig. 5 where dechlorination slow down almost to a stop and was the most inhibited among the anionic species studied here. However, such high pH conditions (~12.5) are very unlikely in natural systems.

### 3.4. Effect of pH

Phosphate buffers were evaluated at 0.05–0.25 M concentrations to control the pH at 2, 7, and 10 based on the  $\text{pK}_a$ 's of the acid and its hydrogen salts. However, the tendency of Mg corrosion to overwhelm the water chemistry meant that the pH rose quickly until it reached a stable value of 10.5 – pH corresponding to a saturated solution of sparingly soluble  $\text{Mg}(\text{OH})_2$ . Further, based on the fact that phosphates were shown to significantly influence dechlorination rates in the Pd/Mg system, they were not a good choice of buffers. In general, choices for a 'neutral' buffer with minimal interference were very limited as most anions signifi-



**Fig. 6.** Plot showing  $\text{NH}_3 - \text{N}$  as it builds-up in the system with time through the reduction of  $\text{NO}_3^-$  by Pd/Mg.

cantly influence Mg corrosion rates. We then tested two biological buffers namely TRIS (2-amino-2-hydroxymethyl-propane-1,3-diol) and HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) which are often used in metal systems where phosphate buffers interfere by forming complexes. TRIS, at a very high concentration of 1 M, was able to control the pH but at these concentrations, dechlorination was seen to be completely inhibited indicating severe interference from TRIS.

Conceptually, in aqueous systems, the  $\text{Mg}(\text{OH})_2$  film quickly reaches an equilibrium with the  $\text{Mg}(\text{OH})_2$  in solution wherein the pH in the vicinity of the film is 10.5, irrespective of the pH in the bulk solution. The point of zero charge of  $\text{Mg}(\text{OH})_2$  is about pH 12. At lower pH's, the potential difference between the surface of  $\text{Mg}(\text{OH})_2$  and the bulk solution can be significant implying that the pH in the vicinity of  $\text{Mg}(\text{OH})_2$  to be higher than the bulk pH [13]. So, while the bulk pH may be as low as 4, the pH in the immediate surroundings of the film surface can be over 10 [9]. Hence, the pH in the vicinity of the  $\text{Mg}(\text{OH})_2$  film is governed by Mg corrosion chemistry and from a practical point of view, pH controlled experiments may have limited importance in predicting the dechlorination behavior at pH's lower than 10.5.

### 4. Conclusions

Ethanol and acetone led to reduced dechlorination rates most likely through reduced hydrogen production and increased affinity of 2-CB for the liquid phase. Acetone also underwent reduction to form 2-propanol, thereby competing for electrons. However, even at high solvent concentrations (up to 50%), the Pd/Mg system was able to bring about 2-CB dechlorination highlighting the robustness of Pd/Mg bimetallic systems.

Among the anions studied here, only  $\text{OH}^-$  produced significant impairment in the reactivity of Pd/Mg systems (at pH > 12) by forming an insoluble film of  $\text{Mg}(\text{OH})_2$ . This suggests that the robust Pd/Mg systems will fare comparably to their bench-scale performance in the presence of naturally occurring anions. Especially interesting results were noted for nitrates, bicarbonates and the sodium salt of humic acid.  $\text{NO}_3^-$  underwent reduction to  $\text{NH}_4^+$  thereby competing for electrons and consequently lowering 2-CB dechlorination rate.  $\text{HCO}_3^-$  was found to significantly enhance 2-CB dechlorination rates, most likely by serving as a proton donor. This suggests enhanced dechlorination performance in natural systems where carbonate species are formed by dissolution of  $\text{CO}_2$ . Humic acid, an important component of natural systems was observed to drastically enhance dechlorination rates, probably by acting as an electron 'shuttle' between the

bimetals and the PCB. Since most anions influenced Mg corrosion, we recommend that caution must be exercised while choosing buffers for Pd/Mg systems. Moreover, we also conclude that systems buffered at pH's lower than 10.5 may provide little practical information as the  $\text{Mg}(\text{OH})_2$  film quickly reaches an equilibrium with its counterpart in solution forcing the pH in the vicinity to 10.5, irrespective of the pH in bulk solution.

### Acknowledgements

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